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(54) Title: DETERGENT COMPOSITIONS

(57) Abstract: A detergent tablet or region thereof of compacted particulate compacted from a particulate composition comprising: a) 25% to 100%wt of the composition of base particles, comprising by weight of themselves: from 15% to 40%wt organic surfactant comprising either (i) no more than 5%wt primary alkyl sulphate or (ii) comprising alkylbenzene sulphonate, from 20% to 60%wt aluminosilicate detergency builder, and from 0 to 60%wt other ingredients, and b) 0 to 75%wt of the composition of other materials mixed with these particles, and wherein the composition comprises from 5% to 60%wt of the composition of sodium tripolyphosphate having at least 50% by weight thereof in the phase I form. The tablets have a good combination of strength and disintegration properties.

DETERGENT COMPOSITIONS

This invention relates to detergent tablets for use in the
5 washing of fabrics. These tablets are intended to disintegrate
completely when placed in water and thus to be consumed in a
single use.

Detergent compositions in tablet form and intended for fabric
10 washing have been described in a number of patent documents
including, for example EP-A-711827, WO-98/42817 and WO-99/20730
(Unilever) and are now sold commercially. Tablets have several
advantages over powdered products: they do not require
measuring and are thus easier to handle and dispense into the
15 washload, and they are more compact, hence facilitating more
economical storage.

Tablets of a detergent composition have frequently been made by
compressing or compacting a composition in particulate form;
20 tablets of the present invention are also made this way.
Although it is desirable that tablets have adequate strength
when dry, yet disperse and dissolve quickly when brought into
contact with water, it can be difficult to obtain both
properties together.

25

Tablets formed using a low compaction pressure tend to crumble
and disintegrate on handling and packing; while more forcefully
compacted tablets may be sufficiently cohesive but then fail to
disintegrate or disperse to an adequate extent in the wash.
30 Tableting will often be carried out with enough pressure to
achieve a compromise between these desirable but antagonistic
properties. However, it remains desirable to improve one or

other of these properties without detriment to the other so as to improve the overall compromise between them.

Organic surfactants function as a binder in tablets and help to plasticise the tablets. However, they can also retard
5 disintegration of the tablet by forming a viscous gel when the tablet comes into contact with water. Thus, the presence of surfactant can make it more difficult to achieve both good strength and speed of disintegration: the problem has proved especially acute with tablets formed by compressing powders
10 comprising organic surfactant and built with insoluble detergency builder such as sodium aluminosilicate (zeolite).

It is already known to make tablets from compositions which consist of (i) base-powder particles which comprise organic
15 surfactant and other materials and (ii) various other ingredients, including water-soluble salts.

It is well known that detergent tablets, like detergent compositions generally, can be made using water-soluble or
20 water-insoluble detergency builder. The water-soluble builder which is commonly used is sodium tripolyphosphate. However it may be necessary to restrict the amount of this material in order to meet regulatory constraints on the amount of phosphate in detergent compositions.

25

The alternative of using a water-insoluble detergency builder, such as zeolite, also encounters problems in that it can be even more difficult to make tablets with satisfactory strength and speed of disintegration.

30

Furthermore, it has been found that the storage stability of some ingredients is not yet optimised in detergent tablets so that the ingredients degrade over time resulting in the tablets

being less effective. Examples of such ingredients include bleaching agents and their activators, and, enzymes.

Current practice in the commercial market in Europe is that
5 when zeolite is used as the detergency builder, some expedient is adopted to assist disintegration. One possibility, is to use a tablet core which is not very strong, but dissolves rapidly, and enclose it in a soluble coating to strengthen the weak tablet core.

10

Other tablets which have been sold commercially and are exemplified in EP-A-838,519 contain a highly soluble salt to promote disintegration. They also utilise zeolite MAP which aids disintegration because it swells on contact with water.
15 However, zeolite MAP is not used by all detergent manufacturers in Europe, and it is not always readily available outside Europe.

WO-A-00/32741, WO-A-98/55590 and WO-A-00/32740 (all Unilever)
20 disclose highly soluble materials such as sodium tripolyphosphate having at least 50% by weight thereof in the phase I form with surfactant granules comprising high levels of organic surfactant which surfactant granules may comprise zeolite.

25

US 4,543,204 (Colgate Palmolive) discloses extruded detergent bars which may comprise sodium tripolyphosphate having a high content of the phase 1 material.

30 WO-A-00/53716 (Henkel) discloses washing tablets comprising non-ionic surfactants, phosphate builders and low levels of zeolite of the Faujasite type, wherein the ratio of non-ionic surfactants: zeolite is between 1:20 and 1:1.

WO-A-01/04256 published 18 January 2001 (Henkel Kommanditgesellschaft Auf Atkien) discloses an auxiliary disintegration agent comprising 20 to 95% wt phosphate and 0.1 to 9%wt zeolite for shaped bodies.

The use of sodium tripolyphosphate having a high content of phase I form in detergent tablets is disclosed in EP-A-839,906 and WO-A-00/77153 (both Unilever). The use of the
10 predominantly phase II form of sodium tripolyphosphate is disclosed in GB-A-2,321,466 (Procter & Gamble) and EP-A-126,963.

[] It is an aim of the present invention to address one or more of
15 the aforementioned technical problems.

We have now discovered how to provide a detergent tablet which comprises a mixture of aluminosilicate builder and organic surfactant and which exhibits good strength and dissolution
20 characteristics. Additionally we have discovered how to provide detergent tablets which provide good storage stability for ingredients which are prone to degradation over time.

Broadly we have found that detergent tablets incorporating base
25 particles which comprise a mixture of aluminosilicate detergency builder and organic surfactant can be made to disintegrate more readily by incorporating in the composition sodium tripolyphosphate having at least 50% of said sodium tripolyphosphate in the phase I form.

30

Thus according to a first aspect of this invention, there is provided a detergent tablet of compacted particulate material

wherein the tablet or a region thereof is compacted from a particulate composition which comprises;

- a) 25% to 100% by weight of the composition of base particles, which particles comprise by weight of themselves:
- 5 from 15% to 40%wt organic surfactant comprising no more than 5% by weight primary alkyl sulphate,
- from 20% to 60%wt aluminosilicate detergency builder, and
- from 0 to 60%wt other ingredients, and
- b) 0 to 75% by weight of the composition of other materials
- 10 mixed with these particles, and
- wherein the composition comprises from 5% to 60% by weight of the composition of sodium tripolyphosphate having at least 50% by weight thereof in the phase I form.

15 According to a second aspect of this invention, there is provided a detergent tablet of compacted particulate material wherein the tablet or a region thereof is compacted from a particulate composition comprising;

- a) 25% to 100% by weight of the composition of base particles,
- 20 which particles comprise by weight of themselves:
- from 15% to 40%wt organic surfactant comprising alkylbenzene sulphonate,
- from 20% to 60%wt aluminosilicate detergency builder, and
- from 0 to 60%wt other ingredients,
- 25 and
- b) 0 to 75% by weight of the composition of other materials mixed with these particles, and
- wherein the composition comprises from 5% to 60% by weight of the composition of sodium tripolyphosphate having at least 50%
- 30 by weight thereof in the phase I form.

The aluminosilicate preferably comprises maximum aluminium zeolite P or zeolite A, more preferably maximum aluminium zeolite P or zeolite 4A, and especially maximum aluminium zeolite P.

5

In especially preferred forms of the invention, the tablet or a region thereof is compacted from a particulate composition which comprises 25% to 95% by weight of the base particles a), maximum aluminium zeolite P as the aluminosilicate and 5 to 75%
10 by weight of the said other materials b).

According to a third aspect of the invention there is provided a method of making a detergent tablet of compacted particulate material, the method comprising the steps of;

- 15 (1) forming detergent base particles comprising (by weight of themselves) 15 to 40%wt organic surfactant with either (i) no more than 5%wt by weight primary alkyl sulphate or (ii) comprising alkylbenzene sulphonate, 20 to 60%wt aluminosilicate detergent builder and 0 to 60%wt other materials, and
20 (2) mixing the base particles with other materials as necessary to form a particulate composition comprising 25 to 100% by weight of the base particles a) and 0 to 75% by weight of the other materials b); and wherein the particulate composition comprises from 5% to 60% by weight thereof sodium
25 tripolyphosphate having at least 50% by weight thereof is in the Phase I form, and
(3) compacting the composition into tablets or regions thereof.

- 30 In an especially preferred method, the base particles a) are prepared by a granulation method and mixed with other materials b) to form a composition comprising 25 to 95% by weight of the base particles and 5 to 75% by weight of the other materials,

with maximum aluminium zeolite P or zeolite A as the aluminosilicate. Preferably the other materials b) comprise from 5% to 60% by weight of the overall composition of sodium tripolyphosphate having at least 50% by weight thereof is in the Phase I form.

These tablets exhibit a good combination of disintegration and strength properties. Furthermore they exhibit good storage stability especially at 37°C, 70% relative humidity for ingredients which are prone to degradation upon tablet storage, especially bleaching agents and their activators, and, enzymes.

This may be utilised to provide tablets comprising zeolite, but without restriction to zeolite MAP as the only form of zeolite which can be used.

Except in the operating and comparative examples, or where otherwise explicitly indicated, all numbers in this description indicating amounts of material or conditions of reaction, physical properties of materials and/or use are to be understood as modified by the word "about." All amounts are by weight, unless otherwise specified.

A detergent tablet may be made from one or more compositions and so may be either homogeneous or heterogeneous. In the present specification, the term "homogeneous" is used to mean a tablet produced by compaction of a single particulate composition, but does not imply that all the particles of that composition will necessarily be of identical composition. The term "heterogeneous" is used to mean a tablet consisting of a plurality of discrete regions, for example layers, inserts or coatings, each derived by compaction from a particulate composition. In a heterogeneous tablet each discrete region of

the tablet will preferably have a mass of at least 10% of the whole tablet, which may be a mass of at least 4 gram.

Where a tablet is a heterogeneous tablet having more than one
5 discrete region, for example a tablet with two layers of different composition, it is possible that one region will be provided by a composition in accordance with this invention while another region will be provided by some other composition. It is also possible that two regions would be
10 provided by different compositions both of which however, embody the present invention.

Base particles

The detergent tablets of the invention comprise compacted
15 particulate material which comprises 25 to 100% by weight of base particles a) and 0 to 75% by weight of other material b) mixed therewith.

Preferably the compositions comprise 30%, 33% or 40% to 60% or
20 70% by weight of base particles a) and 30% or 40% to 60%, 67%, or 70% by weight of other material b). The compositions may comprise for example from 35% to 98%wt of the base particles a) and from 2% to 65%wt of the other materials b).

25 The base particles may be made by spray-drying as described in EP 839906 and WO 98/42819. Alternatively they may be made by a granulation process. For example, EP 838519 and WO 99/20730 describe tablets containing granulated particles in which detergent active (i.e. organic surfactant) is mixed with
30 zeolite A24. This form of zeolite, also known as zeolite MAP, is a special form of zeolite which is the subject of EP-A-384070.

If the base particles a) do not comprise the sodium tripolyphosphate, they can be made by a spray-drying process. However, granulation is the most appropriate method of preparation and is preferred whether the particles comprise 5 sodium tripolyphosphate or not. A suitable method of granulating is disclosed in WO 00/77147 (Unilever).

Organic surfactant

One or more organic detergent surfactants are present in the 10 base particles a) and preferably provide from 7 to 40% by weight of the total composition, more preferably from 8, 10 or 12% by weight of the overall composition up to 40% by weight.

Organic surfactant may be present solely in the base particles 15 a), or some may additionally be present as part of the other material b). Preferably at least 80%, better 90%wt of the organic surfactant in the composition is present in the base particles.

20 The organic surfactant in the base particles preferably comprises anionic surfactant, either alone or mixed with nonionic surfactant.

Anionic surfactant may be present in an amount from 0.5 to 40% 25 by weight, preferably from 2% or 4% up to 30% or 40% by weight of the total composition.

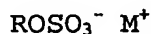
Synthetic (i.e. non-soap) anionic surfactants are well known to those skilled in the art. Examples include alkylbenzene 30 sulphonates, olefin sulphonates, alkane sulphonates, dialkyl sulposuccinates, and fatty acid ester sulphonates.

in which R is alkyl of 6 to 18 carbon atoms R¹ is methyl or ethyl and M⁺ is a solubilising cation.

The amount of non-soap anionic surfactant preferably lies in a range from 5 or 10% to 20 or 25 %wt of the overall tablet composition. The amount of non-soap anionic surfactant in the base particles a) preferably lies in a range from 10 to 40%wt of the weight of the particles themselves, preferably 15 to 35%wt, more preferably 18 to 30wt%.

10

Primary alkyl sulphate having the formula;

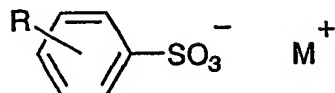


15 in which R is an alkyl or alkenyl chain of 8 to 18 carbon atoms especially 10 to 14 carbon atoms and M⁺ is a solubilising cation, is also commercially significant as an anionic surfactant.

20 In the first aspect of the invention, it is preferred that the base particles a) are substantially free of primary alkyl sulphate. In the second aspect, it is preferred that the base particles a) comprise no more than 5%wt of primary alkyl sulphate based on the weight of these particles and especially
25 that they are substantially thereof. Primary alkyl sulphate may still be added to the composition as part of the other material b). If added, it may be present in an amount as specified above for the non-soap anionic surfactant.

30 It has been found that detergent tablets comprising protease enzyme and low levels, or no, primary alkyl sulphate in the base particles a) exhibit improved stability of protease upon

Linear alkyl benzene sulphonate of the formula:

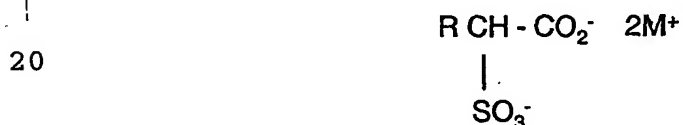


5 where R is linear alkyl of 8 to 15 carbon atoms and M^+ is a solubilising cation, especially sodium, is also a commercially significant anionic surfactant.

It is preferred that the organic surfactant comprises
10 alkylbenzene sulphonates, particularly sodium linear alkylbenzene sulphonates having an alkyl chain length of $\text{C}_8\text{-C}_{15}$.

Such linear alkyl benzene sulphonates are usually the desired
anionic surfactant and may provide 75 to 100 wt% of any anionic
15 non-soap surfactant in the composition.

Further anionic surfactants which may be used are fatty acyl
ester sulphonates of formula:



in which R is an alkyl or alkenyl chain of 8 to 18 carbon atoms
and M^+ is a solubilising cation.

25 Various other anionic surfactants are available and can be used. Examples include olefin sulphonates of formula:



storage compared to detergent tablets which comprise higher amounts of this type of surfactant in the base particles a).

It may also be desirable to include one or more soaps of fatty acids. These are preferably sodium soaps derived from naturally occurring fatty acids, for example, the fatty acids from coconut oil, beef tallow, sunflower or hardened rapeseed oil.

10 Suitable non-ionic surfactant compounds which may be used include in particular the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example, aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide.

15 Specific non-ionic surfactant compounds are alkyl (C₈₋₂₂) phenol-ethylene oxide condensates, the condensation products of linear or branched aliphatic C₈₋₂₀ primary or secondary alcohols with ethylene oxide, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylene-diamine.

Especially preferred are the primary and secondary alcohol ethoxylates, especially the C₉₋₁₁ and C₁₂₋₁₅ primary and secondary 25 alcohols ethoxylated with an average of from 2 to 20 moles of ethylene oxide per mole of alcohol, preferably 5 to 9 moles. Of these the C₉₋₁₁ and C₁₂₋₁₅ primary and secondary alcohols ethoxylated with an average of from 5, 6, 7 or 8 moles of ethylene oxide per mole of alcohol are especially preferred.

30 Preferably the compositions comprise less than 2% by weight, based upon the total weight of the composition, more preferably less than 1 %wt, of C₉₋₁₁ and/or C₁₂₋₁₅ primary and secondary

alcohols ethoxylated with an average of 4 or less moles of ethylene oxide per mole of alcohol. Most preferably the compositions are substantially free of said primary and secondary ethoxylated alcohols.

5

The amount of non-ionic surfactant may lie in a range of from 2 to 40%, better 2.5 or 3% up to 20%wt of the composition. Many non-ionic surfactants are liquids and may be absorbed onto particles of the composition prior to compaction into tablets.

10

When both anionic and nonionic surfactants are used as the organic surfactant, the weight ratio of anionic surfactant: nonionic surfactant is preferably in the range from 4:1 to 1:2, more preferably 3:1 to 1:1.5, most preferably 2.5:1 to 1:1.2.

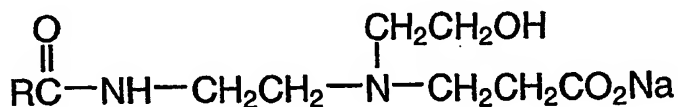
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A mixture of a linear alkylbenzene sulphonate having an alkyl chain length of C₈-C₁₅, especially sodium, with a C₉₋₁₁ or C₁₂₋₁₅ primary or secondary alcohol ethoxylated with an average of from 5 to 9 moles of ethylene oxide per mole of alcohol is

20 especially preferred.

Amphoteric surfactants which may be used jointly with anionic or non-ionic surfactants or both include amphopropionates of the formula:

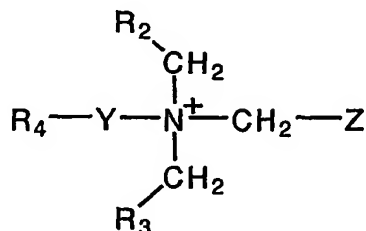
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where RCO is a acyl group of 8 to 18 carbon atoms, especially
30 coconut acyl.

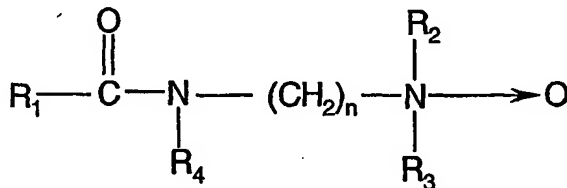
The category of amphoteric surfactants also includes amine oxides and also zwitterionic surfactants, notably betaines of the general formula:

5



10 where R_4 is an aliphatic hydrocarbon chain which contains 7 to 17 carbon atoms, R_2 and R_3 are independently hydrogen, alkyl of 1 to 4 carbon atoms or hydroxyalkyl of 1 to 4 carbon atoms such as CH_2OH , Y is CH_2 or of the form $\text{CONHCH}_2\text{CH}_2\text{CH}_2$ (amidopropyl betaine); Z is either a COO^- (carboxybetaine), or of the form
15 $\text{CHOHCH}_2\text{SO}_3^-$ (sulfobetaine or hydroxy sultaine).

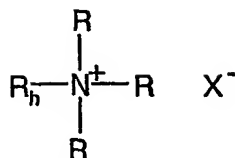
Another example of amphoteric surfactant is amine oxide of the formula;



20 where R_1 is C_{10} to C_{20} alkyl or alkenyl; R_2 , R_3 and R_4 are each hydrogen or C_1 to C_4 alkyl, while n is from 1 to 5.

Cationic surfactants may possibly be used. These frequently have a quaternised nitrogen atom in a polar head group and an
25 attached hydrocarbon group of sufficient length to be hydrophobic. A general formula for one category of cationic surfactants is;

15



where each R independently denotes an alkyl group or hydroxyalkyl group of 1 to 3 carbon atoms and R_h denotes an aromatic, aliphatic or mixed aromatic and aliphatic group of 5 to 24 carbon atoms, preferably an alkyl or alkenyl group of 8 to 22 carbon atoms and X⁻ is a counterion.

The amount of amphoteric surfactant, if any, may be from 3% to 20 or 30% by weight of the tablet or region of a tablet, the amount of cationic surfactant, if any, may be from 0.5% to 10 or 20% by weight of the tablet or region of a tablet.

Granulated base particles a) may provide at least 50% or even more such as at least 52 or at least 55% of the tablet or tablet region. In such a case the concentration of surfactant in the tablet or region may be substantial such as from 15% to 40% by weight of the tablet or tablet region. It is preferred that the amount of total organic surfactant in the tablet or region thereof is at least 10% or 12% by weight in any event.

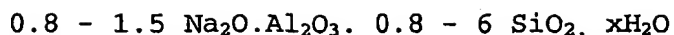
Aluminosilicate detergency builder

The base particles comprise 20 to 60% by weight of aluminosilicate detergency builder.

25

Alkali metal aluminosilicates are strongly favoured as environmentally acceptable water-insoluble softening agents (detergency builders) for fabric washing. Alkali metal (preferably sodium) aluminosilicates may be either crystalline or amorphous or mixtures thereof, having the general formula:

30



These materials contain some bound water (indicated as $x\text{H}_2\text{O}$) and
5 are required to have a calcium ion exchange capacity of at
least 50 mg CaO/g. The preferred sodium aluminosilicates
contain 1.5-3.5 SiO_2 units (in the formula above). Both the
amorphous and the crystalline materials can be prepared readily
by reaction between sodium silicate and sodium aluminate, as
10 amply described in the literature. They remove calcium ions
from water by ion exchange.

The aluminosilicate detergency builder may zeolite P, A, X or Y
and mixtures thereof, with zeolite P and zeolite A being
15 preferred.

Zeolite A is one, well known, form of crystalline sodium
aluminosilicate. Zeolite A may be used even though it does not
assist disintegration and it is readily available. Zeolite 4A
20 has been found to be especially suitable.

Zeolite P is especially preferred. A type of zeolite P known
as zeolite MAP, or maximum aluminium zeolite P (e.g. DOUCIL A24
ex Ineos Silicas, UK), has been found to be especially
25 effective.

The base particles a) preferably comprise aluminosilicate
detergency builder in an amount from 20, 30 or 35% to 40 or 55%
by weight of these particles.

Sodium Tripolyphosphate

The detergent tablet compositions comprises from 5% to 60% by weight of the composition of sodium tripolyphosphate having at least 50% by weight thereof in the phase I form.

5

Sodium tripolyphosphate is very well known as a sequestering builder in detergent compositions. It exists in a hydrated form and two crystalline anhydrous forms. These are the normal crystalline anhydrous form, known as phase II which is the low
10 temperature form, and phase I which is stable at high temperature. The conversion of phase II to phase I proceeds fairly rapidly on heating above the transition temperature, which is about 420°C, but the reverse reaction is slow. Consequently phase I sodium tripolyphosphate is metastable at
15 ambient temperature. The resulting product is generally a mixture of the Phase I and Phase II forms.

Phase I material is known to hydrate to the hexahydrate more rapidly than phase II material. It is also known to dissolve
20 somewhat more rapidly when there is no obstacle to dispersion in the solution. However, during dissolution, this phase I material can form a viscous or solid mass which, in a confined space can hinder dissolution. For instance when making a slurry for spray drying, phase I tripolyphosphate can form so-called
25 "grit", which is a mass of interlocked crystals.

Preferably at least 70%wt, more preferably at least 80%wt, most preferably substantially all of said sodium tripolyphosphate is in the phase I form.

30

It is preferred that the sodium tripolyphosphate which is at least partially in the Phase I form, is also partially hydrated. The extent of hydration is desirably at least 0.5%wt

e.g., 1 to 4% by weight, preferably 2 to 4% by weight of the tripolyphosphate. The extent of hydration may extend up to at least 5% or at least 10% by weight.

- 5 Suitable sodium tripolyphosphate is commercially available. Suppliers include Courbevoie, France and Rhodia, UK.

A process for the manufacture of particles containing a high proportion of the Phase I form sodium tripolyphosphate by spray
10 drying below 420°C is given in US-A-4536377.

The sodium tripolyphosphate in the tablet or region thereof may consist partly of sodium tripolyphosphate which comprises the Phase I form and partly of some other form of sodium
15 tripolyphosphate provided the overall amount of tripolyphosphate complies with the requirement that at least 50% of it is in the Phase I form. For instance, the base particles might comprise sodium tripolyphosphate in which the content of Phase I form was well above 50% by weight of that
20 tripolyphosphate while the composition of the tablet or region also comprises additional sodium tripolyphosphate which is in the anhydrous Phase II form.

The sodium tripolyphosphate is preferably hydrated by a process
25 which leads to a homogenous distribution of the water of hydration within the tripolyphosphate. This can be accomplished by exposing anhydrous sodium tripolyphosphate to steam or moist air.

30 The sodium tripolyphosphate is preferably in a porous form so as to have high surface area. This can be achieved by spray drying the tripolyphosphate. Porosity can be enhanced by spray drying the tripolyphosphate as a mixture with a blowing agent,

that is a compound such as ammonium carbonate which decomposes to yield a gas during the course of the spray drying. This gives the dried material a higher surface area than porous beads of tripolyphosphate obtained without blowing agent.

5

Particles of sodium tripolyphosphate preferably have a small mean particle size, such as not over 300 μ m, preferably 280 μ m or less. Small particle size can, if necessary, be achieved by grinding.

10

Uniform prehydration, high Phase I content, porosity and small particle size all promote rapid hydration when the tripolyphosphate comes into contact with water. A standard test for the rapidity of hydration is the Olten test. It is desirable that in such a test the tripolyphosphate reaches 90% of the final value (i.e. 90% of complete hydration when exposed to water at 80°C) within 60 seconds.

"Rhodiaphos HPA 3.5" is a grade of sodium tripolyphosphate from Rhodia-Chemie (previously from Rhone-Poulenc) which has been found to be particularly suitable. It consists of porous particles of small particle size (mean size below 250 μ m) with 70% Phase I and prehydrated with 3.5% water of hydration.

25 If the base particles a) include some of the sodium tripolyphosphate then it is typically in an amount of from 7-40% of their own weight. However in some aspects of the invention it is preferred that the base particles a) comprise less than 10% of the sodium tripolyphosphate, more preferably less than 5%wt of their own weight, especially less than 2%wt and most especially are substantially free thereof. The remainder of the sodium tripolyphosphate is present in the other particles b).

In some aspects of the invention the other material b) preferably comprises at least 60% by weight, more preferably at least 80% by weight, and especially substantially all of the sodium tripolyphosphate present in the whole composition of the tablet or region thereof.

Preferably the total amount of the sodium tripolyphosphate in the total composition is at least 15% by weight, better in a range from 20 or 25 to 50% by weight.

The preferred weight ratio of the sodium tripolyphosphate: aluminosilicate builder is in the range of from 3:1 to 2:5, better 2.5:1 to 1:1.5, especially 2.2:1 to 1:1.

15

Materials which may be used in tablets or regions of tablets will now be discussed in greater detail, and specific possibilities will be mentioned by way of example.

20 All detergent tablets according to the invention may comprise disintegrant materials to aid in the disintegration of the tablets. If present, the amount is preferably in the range of from 2% to 10% by weight of the composition. These materials are preferably added as part of the other materials (b).

25

Optional water soluble material

In certain forms of the invention, the tablet or region thereof comprises from 35% to 98% by weight of granulated base particles mixed with 2 to 10% by weight of further disintegrant materials (and optionally other ingredients up to 100%wt as appropriate).

The tablets of this invention optionally comprise from 2% to 10% of a material, such as a salt, which has a solubility in deionised water at 20°C of at least 50 grams per 100 grams of water. Preferably amounts of from 2 to 5 or 7% by weight are used. The highly soluble material may be included in the base particles a) or as part of the material b).

A solubility of at least 50 grams per 100 grams of water at 20°C is an exceptionally high solubility: many materials which are classified as water soluble are less soluble than this.

Some suitable highly water-soluble materials are listed below, with their solubilities expressed as grams of solid to form a saturated solution in 100 grams of water at 20°C:-

15

<u>Material</u>	<u>Water Solubility (g/100g)</u>
Sodium citrate dihydrate	72
Potassium carbonate	112
Sodium acetate	119
20 Sodium acetate trihydrate	76
Magnesium sulphate 7H ₂ O	71
Urea	>100

By contrast the solubilities of some other common materials at 25 20°C are:-

<u>Material</u>	<u>Water Solubility (g/100g)</u>
Sodium chloride	36
Sodium sulphate decahydrate	21.5
30 Sodium carbonate anhydrous	8.0
Sodium percarbonate anhydrous	12
Sodium perborate anhydrous	3.7

Sodium tripolyphosphate anhydrous 15

Preferably this highly water soluble material is incorporated as particles thereof in a substantially pure form (i.e. each
5 such particle contains over 95% by weight of the material). However, the said particles may comprise material of such solubility in a mixture with other material, provided that material of the specified solubility provides at least 40% by weight of these particles.

10

Preferred materials are sodium acetate in a partially or fully hydrated form, urea or sodium citrate dihydrate.

Optional water-swellable disintegrant

15 Another material which may be present is a water-swellable but dispersible material.

A number of water-insoluble, water-swellable materials are known to be useful as tablet disintegrants, in particular for
20 pharmaceutical tablets. Although insoluble, these materials are generally dispersible in water. A discussion of such materials is found in "Drug Development and Industrial Pharmacy", Volume 6, pages 511-536 (1980). Such materials are mostly polymeric in nature and many of them are of natural
25 origin. Such disintegrants include starches, for example, maize, rice and potato starches, and starch derivatives, such as Primojel™, and Explotab™, which are both forms of sodium carboxymethyl starch also known as sodium starch glycolate; celluloses, for example Arbocel®-B and Arbocel®-BC (beech
30 cellulose), Arbocel®-BE (beech-sulphite cellulose), Arbocel®-B-SCH (cotton cellulose), Arbocel®-FIC (pine cellulose) as well as further Arbocel® types from Rettenmaier and cellulose derivatives, from example Courlose™ and Nymcel™, sodium

carboxymethyl cellulose, Ac-di-Sol™ cross-linked modified cellulose, and Hanfloc™ microcrystalline cellulosic fibers; and various synthetic organic polymers.

- 5 Cellulose-containing fibrous materials originating from timber may be compacted wood pulps. So-called mechanical pulps generally incorporate lignin as well as cellulose whereas chemical pulps generally contain cellulose but little of the original lignin remains. Pulp obtained by a mixture of
10 chemical and mechanical methods may retain some but not all of the original lignin.

Suppliers of water-swellaable disintegrant materials include Rettenmaier in Germany and FMC Corporation in USA.

15

Other suitable disintegrants include granules based upon water swellaable inorganic materials such as aluminosilicates.

- The impregnated swellaable material which is incorporated into a
20 tablet composition may well have a mean particle size in a range from 250 μ m to 1,500 μ m, more preferably from 700 μ m to 1,100 μ m.

Optional bleach system

- 25 Tableted compositions according to the invention may be bleach-free or may contain a bleach system. If present, this preferably comprises one or more peroxy bleach compounds, for example, inorganic persalts or organic peroxyacids, which may be employed in conjunction with activators to improve bleaching
30 action at low wash temperatures. Preferred inorganic persalts are sodium perborate monohydrate and tetrahydrate, and sodium percarbonate, advantageously employed together with an activator. If any peroxygen compound is present, the amount is

likely to lie in a range from 5 to 50% by weight of the composition, preferably 10 to 20%.

Bleach activators, also referred to as bleach precursors, have been widely disclosed in the art. Preferred examples include peracetic acid precursors, for example, tetraacetylene diamine (TAED), now in widespread commercial use in conjunction with sodium perborate; and perbenzoic acid precursors. N-alkyl ammonium acetonitriles as described in WO 96/40061 and US 6 225 274 may be used as may sodium nonanoyloxy benzene sulphonate (SNOBS) and (6-nonanamidocaproyl)oxy benzene sulphonate (Na.COBS) as described in US 6 207 632 and EP 170 386. The quaternary ammonium and phosphonium bleach activators disclosed in US 4751015 and US 4818426 (Lever Brothers Company) are also of interest. Another type of bleach activator which may be used, but which is not a bleach precursor, is a transition metal catalyst as disclosed in EP-A-458397, EP-A-458398 and EP-A-549272.

A bleach system may also include a bleach stabiliser (heavy metal sequestrant) such as ethylenediamine tetramethylene phosphonate, diethylenetriamine pentamethylene phosphonate or ethylene diamine di-succinate.

If a bleach system is present, the bleach and/or activator are is preferably included as the other material b) mixed with the base particles a).

Other optional materials

Other materials which may be present, typically as 0.5 to 5% of the composition are one or more polycarboxylate polymers, more especially polyacrylates and acrylic/maleic copolymers which

have some function as water-softening agents and also inhibit unwanted deposition onto fabric from the wash liquor.

Tablets may comprise one of the detergency enzymes well known in the art for their ability to degrade and aid in the removal of various soils and stains. Suitable enzymes include the various proteases, cellulases, lipases, amylases, and mixtures thereof, which are designed to remove a variety of soils and stains from fabrics. Examples of suitable proteases are Maxatase™, as supplied by Gist-Brocades N.V., Delft, Holland and Alcalase™, and Savinase™, as supplied by Novo Industri A/S, Copenhagen, Denmark. Detergency enzymes are commonly employed in the form of granules or marumes, optionally with a protective coating, in amount of from about 0.1% to about 3.0% by weight of the composition; and these granules or marumes present no problems with respect to compaction to form a tablet.

The compositions of the invention have been found to be particularly advantageous for the storage stability of protease enzymes. Thus protease enzymes are especially preferred.

Tablets may also comprise a fluorescer (optical brightener), for example, Tinopal™ DMS or Tinopal CBS available from Ciba-Geigy AG, Basel, Switzerland. Tinopal DMS is disodium 4,4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylamino) stilbene disulphonate; and Tinopal CBS is disodium 2,2'-bis-(phenylstyryl) disulphonate.

An antifoam material may be included. Suitable antifoam materials are usually in granular form, such as those described in EP 266863A (Unilever). Such antifoam granules typically comprise a mixture of silicone oil, petroleum jelly,

hydrophobic silica and alkyl phosphate as antifoam active material, sorbed onto a porous absorbed water-soluble carbonate-based inorganic carrier material. Antifoam granules may be present in an amount up to 5% by weight of the composition.

It may also be desirable that a tablet includes an amount of an alkali metal silicate, particularly sodium ortho-, meta- or disilicate. The presence of such alkali metal silicates at levels, for example, of 0.1 to 10 wt%, may be advantageous in providing protection against the corrosion of metal parts in washing machines, besides providing some measure of building and giving processing benefits in manufacture of the particulate material which is compacted into tablets. A composition for fabric washing will generally not comprise more than 15 wt% silicate.

Further ingredients which can optionally be employed in fabric washing detergent tablets of the invention include anti-redeposition agents such as sodium carboxymethylcellulose, straight-chain polyvinyl pyrrolidone and the cellulose ethers such as methyl cellulose and ethyl hydroxyethyl cellulose, fabric-softening agents; heavy metal sequestrants such as EDTA; perfumes; and colorants or coloured speckles.

A number of these further ingredients are typically used in small amounts such as not more than 5% by weight of the tablet or tablet region. They may be incorporated amongst the post-dosed constituents of the composition. Some of them, notably fluorescer, polycarboxylate polymers and anti-redeposition agents may be incorporated into the granulated particles. Any constituents which are liquids such as non-ionic detergents or perfumes may possibly be incorporated within the granulated

particles or may be sprayed onto those particles or the overall mixture. Preferably perfumes are sprayed onto the overall mixture so that they are the last ingredient added to the overall composition before tableting.

5

Granulation of particles

The preparation of detergent compositions in particulate form by granulation processes is well known. A granulation process for making particles which comprise surfactant, zeolite and
10 water-soluble salts is described in EP-A-340013 for example.

Continuous processes for the preparation of granulated particles containing organic surfactant zeolite and other ingredients have been described in EP-A-420317 and WO 98/11193.

15

Processes as described in the above documents can be modified to include sodium tripolyphosphate among the solids supplied to the granulation process to produce the base particles a).

20 A suitable method of granulating is disclosed in WO 00/77147 (Unilever) wherein a liquid binder is contacted with a solid starting material in a high-speed mixer and the resulting mixture treated in a medium- or low-speed mixer and finally in a gas fluidisation granulator, where more liquid binder is
25 added.

After granulation the particles may have average particle size in the range from 200 to 2000µm, more preferably from 250 to 1400µm. Fine particles, such as those smaller than 180µm or
30 200µm and oversized particles may be eliminated by sieving before tableting, if desired, although we have observed that this is not always essential. Sieved out particles may be returned to the granulation stage if oversized.

The starting particulate composition may suitably have a bulk density of at least 500g/litre, preferably at least 600g/litre, and possibly at least 700g/litre.

5

Tableting

Tableting entails compaction of a particulate composition. A variety of tableting machinery is known, and can be used.

Generally it will function by stamping a quantity of the
10 particulate composition which is confined in a die.

The mould in which the tablet is formed may be provided by an aperture within a rigid structure and a pair of dies which can be urged into the aperture towards each other, thereby

15 compacting the contents of the aperture. A tableting machine may have a rotary table defining a number of apertures each with a pair or associated dies which can be driven into an apertures. Each die may be provided with an elastomeric layer on its surface which contacts the tablet material, as taught in
20 WO 98/46719 or WO 98/46720.

Tableting may be carried out at ambient temperature or at a temperature above ambient which may allow adequate strength to be achieved with less applied pressure during compaction. In
25 order to carry out the tableting at a temperature which is above ambient, the particulate composition is preferably supplied to the tableting machinery at an elevated temperature. This will of course supply heat to the tableting machinery, but the machinery may be heated in some other way also.

30

When the sodium tripolyphosphate is present in the base particles a method of forming the detergent composition comprises;

- (1) forming detergent base particles by mixing together and
5 granulating 15 to 40% by weight of organic surfactant, 20 to 60% by weight of aluminosilicate detergency builder, 7 to 40% by weight of sodium tripolyphosphate, at least 50% of which is in Phase I form, and optionally 0 to 58% of other ingredients;
- (2) optionally mixing these detergent base particles with
10 other ingredients which may include sodium tripolyphosphate, so as to form a composition comprising 33 to 100% by weight of base particles and 0 to 67% by weight of other ingredients, wherein the composition comprises from 5 to 50% by weight of sodium tripolyphosphate having at least 50% in the Phase I
15 form, and
- (3) compacting that composition into tablets or regions thereof.

If any heat is supplied, it is envisaged that this will be
20 supplied conventionally, such as by passing the particulate composition through an oven, rather than by any application of microwave energy.

The size of a tablet will suitably range from 10 to 160 grams,
25 preferably from 15 to 60g, depending on the conditions of intended use, and whether it represents a dose for an average load in a fabric washing or dishwashing machine or a fractional part of such a dose. The tablets may be of any shape. However, for ease of packaging they are preferably blocks of
30 substantially uniform cross-section, such as cylinders or cuboids.

The overall density of a tablet for fabric washing preferably lies in a range from 1000 or 1040g/litre up to 1400 or 1450 g/litre. The overall density of a tablet of some other cleaning composition, such as a tablet for machine dishwashing or as a
 5 bleaching additive, may range up to 1700gm/litre and will often lie in a range from 1300 to 1550gm/litre.

The invention will now be further illustrated with reference to the following non-limiting examples. Further examples will be
 10 apparent to the person skilled in the art.

EXAMPLES

Example 1

Tablets for use in fabric washing were made, starting with a
 15 granulated base powder of the following composition:

Ingredient	% by weight
Sodium linear alkylbenzene sulphonate	22
C ₁₃₋₁₅ fatty alcohol 7EO	5
Zeolite 4A	29
Sodium carbonate (light)	27
Sodium tripolyphosphate	12.5
Moisture and minor ingredients	4.5
Total	100%

Particulate compositions were made by mixing this powder with further ingredients as tabulated below.

Ingredient	% By Weight
Base powder	56
Sodium tripolyphosphate (HPA 3.5)	35
Primary alkyl sulphate particles	5.5
Coloured speckles	1.5
Enzymes, heavy metal sequestrant and perfume	2
Total	100%

In the above composition, the sodium tripolyphosphate in the granulated base powder was anhydrous sodium tripolyphosphate consisting predominantly of the Phase II anhydrous form.

- 5 The sodium tripolyphosphate which was mixed with the granulated base powder particles comprised over 75% of its own weight in the Phase I form and was partially hydrated to contain 3.5% of its own weight of water of hydration. This sodium tripolyphosphate was supplied by Rhodia Chemie under their
10 designation Rhodiaphos HPA 3.5 and it had a porous structure resulting from the spray-drying procedure employed prior to partial hydration.

The composition was sieved to remove all particles smaller than
15 250µm or larger than 1400µm. Then 40g portions of the composition were compacted into tablets of 44mm diameter using a hand press.

To test dissolution of tablets, a test procedure was used in
20 which a tablet was placed on a plastic sieve with 2mm mesh size which was immersed in 9 litres of demineralised water at ambient temperature of 20°C. The water conductivity was monitored until it reached a constant value. The time for dissolution of the tablets was taken as the time (T_{90}) for
25 change in the water conductivity to reach 90% of its final magnitude; and was found to be 3.5 minutes.

The strength of the tablets was measured by compressing them radially, between the platens of a universal materials testing
30 machine until fracture of the tablet occurred.

The force at the fracture was measured. From this measurement of force a test parameter called diametral fracture stress, which we have used in the past, can be calculated using the equation:

5

$$\sigma = \frac{2F_f}{\pi Dt}$$

where σ is the diametral fracture stress in Pascals, F_f is the
 10 applied force in Newtons to cause fracture, D is the tablet diameter in meters and t is the tablet thickness in meters. The value of DFS measured for these tablets was 40 kPa. (It is desirable that the value of DFS is at least 20 or 25kPa).

15 Example 2

A spray-dried base powder of the following composition was prepared:

Ingredients	% By Weight
Linear alkyl benzene sulphonate	22
Nonionic detergent (C ₁₃₋₁₅ fatty alcohol 7EO)	5
Soap	3
Zeolite 4A	35
Sodium carbonate	20
Sodium tripolyphosphate (fully hydrated)	10
Moisture and other minor ingredients	5
Total	100%

This powder was mixed with other materials as follows:

Ingredients	% by weight
Base powder	66
Sodium tripolyphosphate (Rhodiaphos HPA 3.5)	31
Blue speckles	1.5
Sequestrant, enzymes and perfume	3.5
Total	100%

20

The resulting compositions was sieved and made into tablets as in Example 1.

Example 3

- 5 Tablets for use in fabric washing were made, starting with a granulated base powder of the following compositions. Example 3A is a comparative example where the base powder particles do not comprise aluminosilicate detergency builder. Example 3 is an example according to the invention.

10

Ingredients	% by weight	% by weight
	Ex 3A	Ex 3
Sodium linear alkyl benzene sulphonate	23.7	20.8
Nonionic detergent (C ₁₃₋₁₅ fatty alcohol 7EO)	5.1	9.2
Nonionic detergent (C ₁₃₋₁₅ fatty alcohol 3EO)	5.3	-
soap	0.7	1.6
zeolite A24 (anhydrous)	-	46.5
70/30 AA/MA co-polymer salt (100%)	3.1	-
Sodium tripolyphosphate	40.6	-
Na acetate 3H ₂ O/ zeolite A24 (99:1wt mix)	-	5.9
light soda ash		6.9
sodium disilicate	8.7	-
SCMC (68% active)	0.5	0.9
Moisture, salts, NDOM	12.3	8.2
Total	100%	100%

Particulate compositions were made by mixing this powder with further ingredients as tabulated below.

Ingredients	% by weight	% by weight
	Ex 3A	Ex 3
Base powder	41.4	42.4
Antifoam granules	2.6	2.1
Sodium tripolyphosphate (Rhodiaphos HPA 3.5)	34.5	32.7
Granular Na-disilicate	-	2.5

(80% active granules)		
TAED (83% active granules)	2.8	2.8
Coated sodium Percarbonate	14.00	14.0
Savinase 12.0T 3250 GU/mg	0.4	0.4
Perfume, heavy metal sequestrant, fluorescer granule	2.8	3.1
Blue Speckles	1.5	-
Total	100%	100%

The sodium tripolyphosphate in the base powder of Example 3A was a mixture of about 55 parts of anhydrous sodium tripolyphosphate phase II and about 45 parts of anhydrous sodium tripolyphosphate phase I. The 70/30 AA/MA co-polymer salt (100%) was Sokalan CP5 (ex BASF).

Comparative example 3B

A further comparative laundry detergent tablet was made from a granulated base powder with the other ingredients added thereto. The amounts are given for the base powder on the basis of the amount of each ingredient present in the final composition.

Example 3B	% by weight
BASE POWDER	
Na Primary alkyl sulphate	8
Nonionic detergent (C ₁₃₋₁₅ fatty alcohol 7EO)	4
soap	1
zeolite A24 (anhydrous)	16
Na acetate 3H ₂ O/ zeolite A24 (99:1wt mix)	3
light soda ash	4
SCMC (68% active)	1
ADDED INGREDIENTS	
Sodium tripolyphosphate (Rhodiaphos HPA 3.5)	31
sodium citrate 2H ₂ O	2

TAED (83% active granules)	6
Coated sodium Percarbonate	16
Savinase 12.0T 3250 GU/mg	1
Perfume, heavy metal sequestrant, polymers, other enzymes, Granular Na-disilicate (80% granules), antifoam granules	7
Total	100%

The resulting compositions were sieved and made into tablets as in Example 1.

5 A quantity of the tablets were packaged in flow-wrap packaging and stored in normal carton packs at 37°C/70 % relative humidity for up to 8 weeks. At the intervals given in the tables below, a tablet was selected and tested for the presence of TAED, protease and percarbonate. The results are given in
 10 the table below. The numbers in the (results) column show the initial level of the ingredient detected in the tablet and the level after the given storage time. The numbers in the (%) column show the percentage of the ingredient remaining after the given storage time, expressed as a percentage of the
 15 original level detected in the tablet. The percarbonate results are expressed as % available oxygen. The protease result is expressed as enzyme activity GU/mg.

TAED storage stability

	storage (wks)	3A (%)	3A (result)	3 (%)	3 (result)
37°C 70% RH	0	100	2.3	100	2.7
	2	83	1.9	89	2.4
	4	74	1.7	78	2.1
	8	57	1.3	78	2.1

Percarbonate storage stability

	storage (wks)	3A (%)	3A (result)	3 (%)	3 (result)
37°C 70% RH	0	100	2.0	100	2.0
	2	87	1.74	92	1.84
	4	85	1.7	90	1.8
	8	70	1.4	85	1.7

Protease (as savinase) storage stability

	storage (wks)	3A (%)	3A (result)	3B (%)	3 (%)	3 (result)
37°C 70% RH	0	100	14.9	100	100	14.4
	2	77	11.5	-	94	13.6
	4	65	9.7	-	85	12.3
	8	30	4.4	50	90	13.0

5

The tablets of the invention show better storage stability at 37°C, 70% relative humidity for TAED, percarbonate and especially for protease enzyme (savinase) than do the tablets comprising no aluminosilicate builder (Ex 3A). They also show better stability for protease than do tablets comprising conventional amounts of primary alkyl sulphate and no linear alkyl benzene sulphonate (Ex 3B).

15

Claims

1. A detergent tablet of compacted particulate material wherein
the tablet or a region thereof is compacted from a
5 particulate composition which comprises;
 - a) 25% to 100% by weight of the composition of base
particles, which particles comprise by weight of themselves:
from 15% to 40%wt organic surfactant comprising no more
than 5% by weight primary alkyl sulphate,
10 from 20% to 60%wt aluminosilicate detergency builder, and
from 0 to 60%wt other ingredients, and
 - b) 0 to 75% by weight of the composition of other
materials mixed with these particles, and
wherein the composition comprises from 5% to 60% by weight
15 of the composition of sodium tripolyphosphate having at
least 50% by weight thereof in the phase I form.

2. A detergent tablet of compacted particulate material
wherein the tablet or a region thereof is compacted from a
20 particulate composition comprising;
 - a) 25% to 100% by weight of the composition of base
particles, which particles comprise by weight of
themselves:
from 15% to 40%wt organic surfactant comprising
25 alkylbenzene sulphonate,
from 20% to 60%wt aluminosilicate detergency builder, and
from 0 to 60%wt other ingredients, and
 - b) 0 to 75% by weight of the composition of other
materials mixed with these particles, and
30 wherein the composition comprises from 5% to 60% by weight
of the composition of sodium tripolyphosphate having at
least 50% by weight thereof in the phase I form.

3. A tablet according to either claim 1 or claim 2 wherein the aluminosilicate detergency builder comprises maximum aluminium zeolite P or zeolite A.
- 5
4. A tablet according to either claim 3 wherein the aluminosilicate detergency builder comprises maximum aluminium zeolite P.
- 10 5. A tablet according to any one of the preceding claims wherein the base particles comprise aluminosilicate detergency builder in an amount from 30% to 55% by weight of these particles.
- 15 6. A tablet according to any one of the preceding claims wherein the base particles comprise less than 5% of their own weight of the sodium tripolyphosphate and the other materials comprise the remainder of the sodium tripolyphosphate.
- 20
7. A tablet according to claim 6 wherein the base particles are substantially free of the sodium tripolyphosphate.
8. A tablet according to any one of the preceding claims
- 25 wherein the sodium tripolyphosphate is partially hydrated.
9. A tablet according to claim 8 wherein the degree of hydration of the sodium tripolyphosphate is from 0.5% to 10% by weight of the sodium tripolyphosphate.

10. A tablet according to any one of the preceding claims wherein the composition comprises from 8% to 40% by weight of organic surfactant.
- 5 11. A tablet according to any one of the preceding claims wherein at least 90% by weight of the organic surfactant in the composition is present in the base particles.
- 10 12. A detergent tablet as claimed in any one of the preceding claims wherein the organic surfactant in the base particles comprises anionic surfactant and nonionic surfactant and the weight ratio of anionic surfactant to the nonionic surfactant is in the range of from 4:1 to 1:2.
- 15 13. A tablet according to claim 2 wherein the base particles comprise no more than 5% by weight primary alkyl sulphate based on the weight of these particles.
- 20 14. A tablet according to any one of the preceding claims wherein the composition comprises from 35% to 98% of the base particles and from 2% to 65% of the other materials.
- 25 15. A tablet according to claim 14 wherein the other materials comprise disintegrant materials in an amount from 2% to 10% by weight of the composition.
- 30 16. A tablet according to claim 15 wherein the disintegrant materials are highly soluble materials selected from sodium citrate dihydrate, potassium carbonate, sodium acetate, sodium acetate trihydrate, urea and magnesium sulphate $7H_2O$.

17. A tablet according to any one of the preceding claims wherein the particulate composition has a mean particle size of between 250 and 1400 μ m.
- 5
18. A tablet according to any one of the preceding claims wherein the tablet or a region thereof is compacted from a composition which comprises 25% to 95% by weight of the base particles and 5 to 75% by weight of the other materials, and wherein the aluminosilicate comprises maximum aluminium zeolite P, and the other materials comprise from 5% to 60% by weight of the overall composition of the sodium tripolyphosphate.
- 10
- 15 19. A tablet according to claim 18 wherein the base particles are prepared by a granulation method.
- 20
20. A method of making a detergent tablet of compacted particulate material, the method comprising the steps of;
- 25
- 20 1) forming detergent base particles comprising by weight of themselves 15 to 40%wt organic surfactant with either (i) no more than 5%wt by weight primary alkyl sulphate or (ii) comprising alkylbenzene sulphonate, 20 to 60%wt aluminosilicate detergency builder and 0 to 60%wt other materials, and
- 30
- 2) mixing the base particles with other materials as necessary to form a particulate composition comprising 25 to 100% by weight of the base particles and 0 to 75% by weight of the other materials and wherein the particulate composition comprises from 5% to 60% by weight thereof sodium tripolyphosphate having at least 50% by weight thereof in the Phase I form, and

3) compacting the composition into tablets or regions thereof.

21. A method according to claim 20, wherein the base particles
5 are prepared by a granulation method and are mixed with
other materials to form a composition comprising 25 to 95%
by weight of the base particles and 5 to 75% by weight of
the other materials, and wherein the aluminosilicate
comprises maximum aluminium zeolite P or zeolite A.

10

22. A method according to either claim 20 or 21 wherein the
other materials comprise from 5% to 60% by weight of the
overall composition of the sodium tripolyphosphate having
at least 50% by weight thereof is in the Phase I form.

15

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24 November 2000 (24.11.2000) EP
0031504.4 22 December 2000 (22.12.2000) GB
01306604.8 1 August 2001 (01.08.2001) EP

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WO 02/042398 A3

(54) Title: DETERGENT COMPOSITIONS

(57) Abstract: A detergent tablet or region thereof of compacted particulate compacted from a particulate composition comprising; a) 25% to 100%wt of the composition of base particles, comprising by weight of themselves: from 15% to 40%wt organic surfactant comprising either (i) no more than 5%wt primary alkyl sulphate or (ii) comprising alkylbenzene sulphonate, from 20% to 60%wt aluminosilicate detergency builder, and from 0 to 60%wt other ingredients, and b) 0 to 75%wt of the composition of other materials mixed with these particles, and wherein the composition comprises from 5% to 60%wt of the composition of sodium tripolyphosphate having at least 50% by weight thereof in the phase I form. The tablets have a good combination of strength and disintegration properties.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 01/13479

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D17/00 C11D3/06 C11D3/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 20730 A (UNILEVER PLC (GB); UNILEVER NV (NL)) 29 April 1999 (1999-04-29) cited in the application page 3, line 19 - line 22 page 5, line 10 - line 23 page 15, line 18 - line 23 page 17, line 1 - line 7 page 22, line 22 -page 23, line 18 claims 1,10; example 1	1-22
P,X	WO 01 38478 A (UNILEVER PLC (GB); LEVER HINDUSTAN LTD (IN); UNILEVER NV (NL)) 31 May 2001 (2001-05-31) page 3, line 16 - line 32 page 2, line 4 - line 11 page 4, line 32 -page 7, line 25 claims 1,4,6; example 3	1-22

☐ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 01/13479

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9920730	A	29-04-1999	AU 725525 B2	12-10-2000
			AU 1030899 A	10-05-1999
			BR 9812955 A	08-08-2000
			CA 2307377 A1	29-04-1999
			CN 1276828 T	13-12-2000
			CZ 20001498 A3	12-09-2001
			WO 9920730 A1	29-04-1999
			EP 1027421 A1	16-08-2000
			HU 0004038 A2	28-03-2001
			PL 340050 A1	15-01-2001
			TR 200001042 T2	21-08-2000
			ZA 9809585 A	25-04-2000
WO 0138478	A	31-05-2001	AU 2002301 A	04-06-2001
			AU 2508801 A	04-06-2001
			WO 0138478 A1	31-05-2001
			WO 0138479 A1	31-05-2001

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